

Measurements and Correlation of Hydrogen-Bonding Vapor Sorption Equilibrium Data of Binary Polymer Solutions

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Vapor sorption equilibrium data of ten binary polymer/solvent systems were measured using sorption equilibrium cell equipped with a vacuum electromicrobalance. Tested solvents were water, methanol, ethanol and n-propanol and polymer solutes were poly(ethylene glycol), poly(ethylene oxide), poly(propylene glycol) and poly(propylene glycol). The measured sorption obtained in the present work, were compared with existing literature data and the degree of reliability of the measured data was discussed. Vapor sorption equilibrium data obtained in the present study were correlated by UNIQUAC model and the multi-fluid non-random lattice fluid hydrogen bonding equation of state (MF-NLF-HB EOS) recently proposed by the present authors

Introduction

Understanding sorption equilibrium characteristics of vapor-phase species in polymers is of prime importance in designing and operating industrial process such as membrane separation of organic from waste streams^{1,2}, pervaporation processes³, separation of organic from polymer products and processing paint and coating agents^{4,5}.

Despite the various sorption equilibria data of polymer solutions were reported in the literature, existing data are frequently available only in a limited range of the

concentration of solvent species.

In the present study, emphasis was given to the measurement of sorption equilibrium data of binary polymer solution containing interaction of hydrogen bonding by an apparatus based on the principle of the vacuum electromicrobalance. Besides, some complimentary measurement of data was made to enhance the utility of the existing systems over an extended range of solvent concentrations. The polymers tested were poly(ethylene glycol) and Poly(ethylene oxide), poly(tetramethylene glycol) and Poly(propylene oxide) and solvents were used water, methanol, ethanol and n-propanol.

To model the measured activity of solvents in polymer solutions, one of well-known g^E model, UNIQUAC⁶ was used. Also, the same data were tried to correlate by the MF-NLF-HB EOS which was recently formulated by the present authors based the multi-fluid approximation of the non-random lattice fluid theory with the combination of the theory of hydrogen bonding after Veytzman⁷.

Experimental Section

1. Materials and apparatus

For polymers, PEG and PPG were purchased from Fluka Chemie AG (Buchs, Switzerland). PEO and PTMG were purchased from Aldrich Co. (St. Louis, MO, United States). The number of average molecular weight (M_n) of PEG was 600, of PPG was 400, of PTMG was 1400, of PEO was 600000. These sample polymers were used directly without further purification. Water, methanol, ethanol and n-propanol were purchased from Aldrich Co. All solvents were HPLC-grade and these were used directly

without further purification.

The schematic diagram of the sorption apparatus used in the experiment is shown in Fig. 1. To reduce flow and thermal fluctuations in the equilibrium cell, the whole unit was immersed in an air-bath. The amount of sorbed solvent to a polymer was measured with a Satorius M25D-V vacuum electromicro-balance [MB], which has the accuracy of $\pm 0.001\text{mg}$ (Goettingen, Germany). A calibrated mass was loaded to the left side of the balance as a reference mass and the polymer sample was put to the right side of the balance. A dish-type quartz sorption cell was used to load the polymer sample. Platinum wire was used to link both arms to the balance for preventing possible oxidative corrosion of the arm by the solvent. Potential leakage of the system was checked by maintaining the pressure under 1.3×10^{-2} Pa for a week using a Precision Science vacuum pump (Chicago, IL, United States).

Water baths were installed in three regions for separately controlling temperature to prevent temperature fluctuation which could result in condensation of solvent on the surface of the sorption cell. Water bath 1 [WB1] which has the accuracy of $\pm 0.01^\circ\text{C}$ (Polyscience 9710, Niles, IL, United States) was used to control the solvent generation part. Since the vaporized solvent at the sorption area must be maintained in a saturated state, an accurate control of temperature was made. Water bath 2 [WB2], which has the accuracy of $\pm 0.01^\circ\text{C}$ (Polyscience 9710) was installed to control the sorption cell. The distribution of temperatures in each water bath was maintained differently such that the temperature of air bath (T_3) > water bath 2 (T_2) > water bath 1 (T_1). Mercury head in the manometer [WM] was measured to within $\pm 0.01\text{mmHg}$ using a cathetometer (Gaertner Scientific, Chicago, United States).

2. Experimental procedure

After a polymer sample was loaded to the sorption cell, valve 3 [V₃] and valve 4 [V₄] were closed. Valve 1 [V₁] and valve 2 [V₂], which were connected to vacuum pump, were opened to create a vacuum state within the cell. Volatile low molecular weight substances and impurities including air were removed from the polymer sample using this way. At the high-vacuum state, if the mass of the polymer sample stayed within the fluctuation range within $\pm 0.001\text{mg}$ for 3 hours, the measurement of the sorption equilibrium was started. To absorb vapor-phase solvent by polymer sample, the valve 1 [V₁], valve 2 [V₂] and valve 3 [V₃] were closed and the valve 4 [V₄] was opened in order to transfer equilibrated vapor from the vapor generation unit. The sorbed solvent was measured with 3min interval by a data processor [PC]. When the mass of absorbed solvent by polymer stayed within the error range of $\pm 0.005 \text{ mg}$ for 3 hours, we assumed that a sorption equilibrium state was reached.

Data reduction and correlation

1. Activities of solvents from experiment

Measured data were the vapor pressure of the solvent, P_1 and the sorbed mass of solvent, w_1 . From these data, the activities of a solvent in a polymer solution were calculated by:

$$a_1 = \frac{P_1}{P_1^{sat}} \exp\left(\frac{B_{11}(P_1 - P_1^{sat})}{RT}\right) \quad (1)$$

where P_1^{sat} is saturation pressure and B_{11} is the second virial coefficient. These values were estimated using existing correlation methods reported in the data book^{8,9}

2. MF-NLF-HB EOS

Measured sorption data were comparatively correlated using UNIQUAC as a g^E model and using MF-NLF-HB EOS. This EOS was proposed recently by the present authors. From the previous work of the present authors^{7,10,11,12}, the MF-NLF-HB EOS for general multi-component hydrogen bonding mixtures is derived by

$$P = \frac{1}{\beta V_H} \left\{ \frac{z}{2} \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] - \ln(1 - \rho) - v_{HB} \rho + \frac{z}{2} \sum_{i=1}^c \theta_i \left(\frac{\tau_{0i}}{\sum_{k=0}^c \theta_k \tau_{ki}} - 1 \right) \right\} \quad (2)$$

where, $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $\rho = \sum \rho_i$, $\rho_i = V_i^* / V$, $V_i^* = N_a r_i V_H$ and x_i is the mole fraction of species i in a mixture. There are apparently four molecular parameters in the EOS for pure fluids; z , V_H , r_1 and ε_{11} . Thus, for a pure fluid we need to determine only two independent molecular parameters, r_1 and ε_{11} . The parameters, r_1 and ε_{11} are regressed at each isotherm and represented as functions of temperature.

$$\varepsilon_{11} / k = E_a + E_b (T - T_0) + E_c [T \ln(T_0 / T) + T - T_0] \quad (3)$$

$$r_1 = R_a + R_b (T - T_0) + R_c [T \ln(T_0 / T) + T - T_0] \quad (4)$$

where $T_0 = 273.15\text{K}$ is a reference temperature.

We have one binary energy parameter λ_{12} for a binary, which is defined by

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}(1 - \lambda_{12}) \quad (5)$$

where λ_{12} is determined by data fitting and may be temperature dependent.

Results and discussion

The sorption equilibrium data were measured by the vacuum electromicrobalance as shown in Fig.1. Measured systems were PEG + n-propanol, PPG + water, PPG + methanol, PPG + ethanol, PEO + water, PEO + methanol, PEO + ethanol, PTMG + water, PTMG + methanol, PTMG + ethanol. Measured data and their experimental conditions were summarized in Table 1.

From the sorption data obtained in the present study and other existing data, the activities of solvents in various polymers were calculated using both UNIQUAC model and MF-NLF-HB EOS. The best-fitted UNIQUAC binary parameters, A_{12} , A_{21} and MF-NLF-HB EOS binary interaction parameters, λ_{12} were summarized in Table 2. Since the PVT data of PPG was not available in literature, the λ_{12} for system with PPG was assumes as zero.

The reliability of the apparatus was repeatedly verified by the present authors and reported them elsewhere. Thus, in this work, by simply choosing PPG + water system, comparison of the data obtained in this work and the data by other investigators¹³ were compared together in Fig. 2. Also, the data were correlated by

UNIQUAC model. In Fig. 3, the measured sorption data of PEO + ethanol system was shown with the correlated results by the UNIQUAC and MF-NLF-HB model. Both models found to be qualitatively useful for the calculation of activities of sorbed species in polymers. However, the MF-NLF-HB model is an EOS which can be used to calculate thermodynamic properties of pure systems and mixtures while the UNIQUAC cannot be used to calculate pure properties. In this regard, EOS approach should be more useful than g^E model approach.

In Figs. 4 and 5, the measured sorption data for PTMG + methanol and PTMG + ethanol system was shown, respectively. As one can see from these figures, the UNIQUAC and the MF-NLF-HB model fit the data equivalently well. Although we omit further graphical demonstration, the two models fit quantitatively well the data of PEG + n-propanol, PEO + methanol systems. Also, in a region of low mass fraction, the activities of alcohols tend to increase with increasing the carbon number. This trend was identically applicable to systems containing PEO, PPG or PTMG.

Concluding Remarks

The sorption data for several solvent-polymer systems with the hydrogen bonding was measured by a vacuum electromicrobalance. Most of the systems chosen in this work, existing data are not available in literatures. Thus, it will be a new release of such data in thermodynamic society. Upon comparative correlation of these sorption data of hydrogen bonding with the UNIQUAC model as a g^E approach and the MF-NLF-HB model as a EOS approach, it was found that both model equivalently fit well the data. However, the EOS approach found to be more versatile than the g^E model

since an EOS approach can be used to calculate other thermodynamic properties of pure compounds.

List of symbols

A_{ij} : binary interaction parameter of UNQUAC

B_{11} : The second virial coefficient.

N_a : Avogadro's number

P : Pressure(kPa)

q_i : surface area parameter

q_M : mole fraction average of q_i

r_i : segment number

r_M : mole fraction average of r_i

R : universal gas constant($\text{Jmol}^{-1}\text{K}^{-1}$)

T : temperature(K)

V : molar volume($\text{cm}^3\text{mol}^{-1}$)

V^* : characteristic volume of component i ($\text{cm}^3\text{mol}^{-1}$)

V_H : volume of a unit cell(cm^3)

z : lattice coordination number

Greek letters

ε_{ij} interaction energy for i - j segment contacts(J)

λ_{ij} binary interaction parameter for i - j contacts

- ρ total segment fraction
- ρ_i segment fraction of component i
- θ_i surface area fraction of component i
- τ_{ij} nonrandomness factor

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Figure 3. Measured and calculated activities of ethanol in PEO at 303.15K.

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Figure 5. Measured and calculated activities of ethanol in PEG at 303.15K.

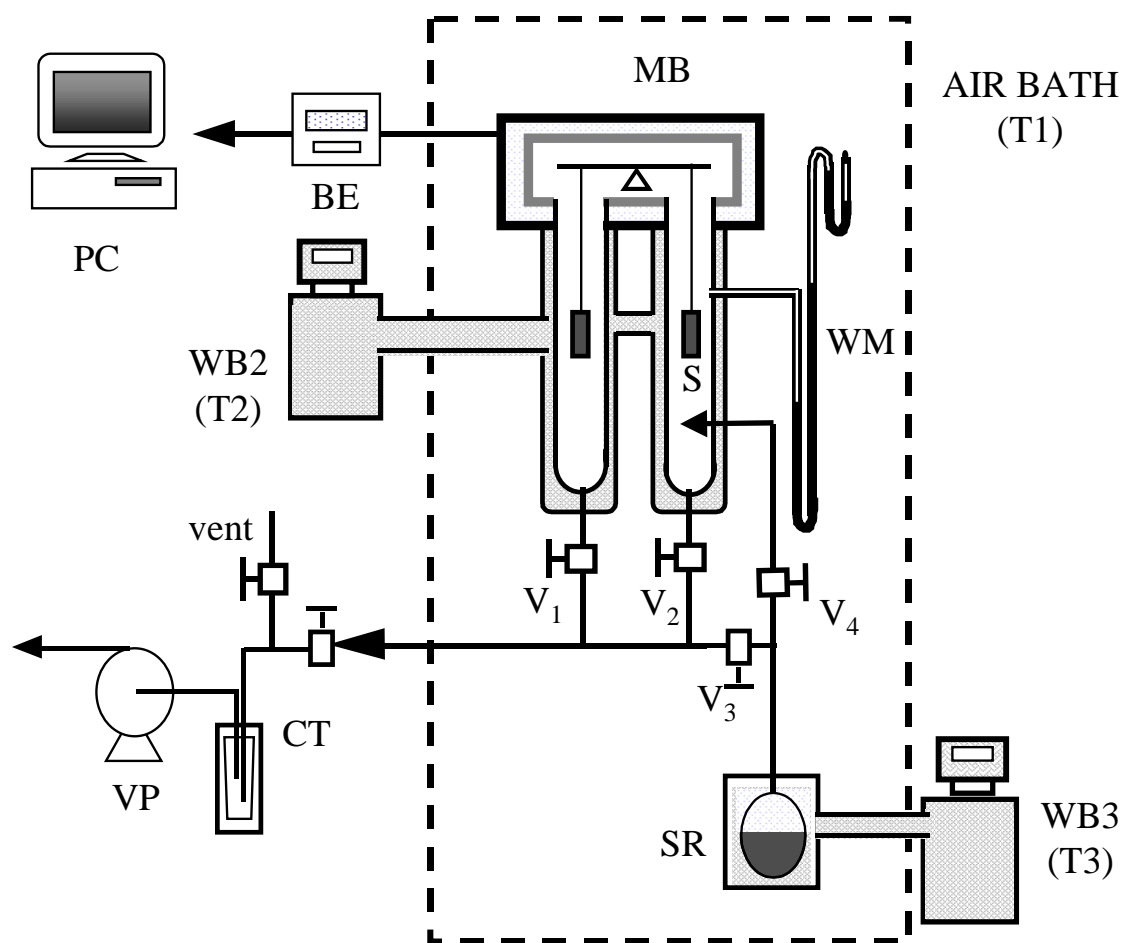


Figure 1. Schematic diagram of vapor sorption apparatus: PC, personal computer; MB, microbalance; BE, balance electronics; WB1(T1), water bath1; WB2 (T2), water bath2; WM, W-tube mercury manometer; S, polymer sample; SV, solvent vessel; CT, cold trap; VP, vacuum pump; V, valve.

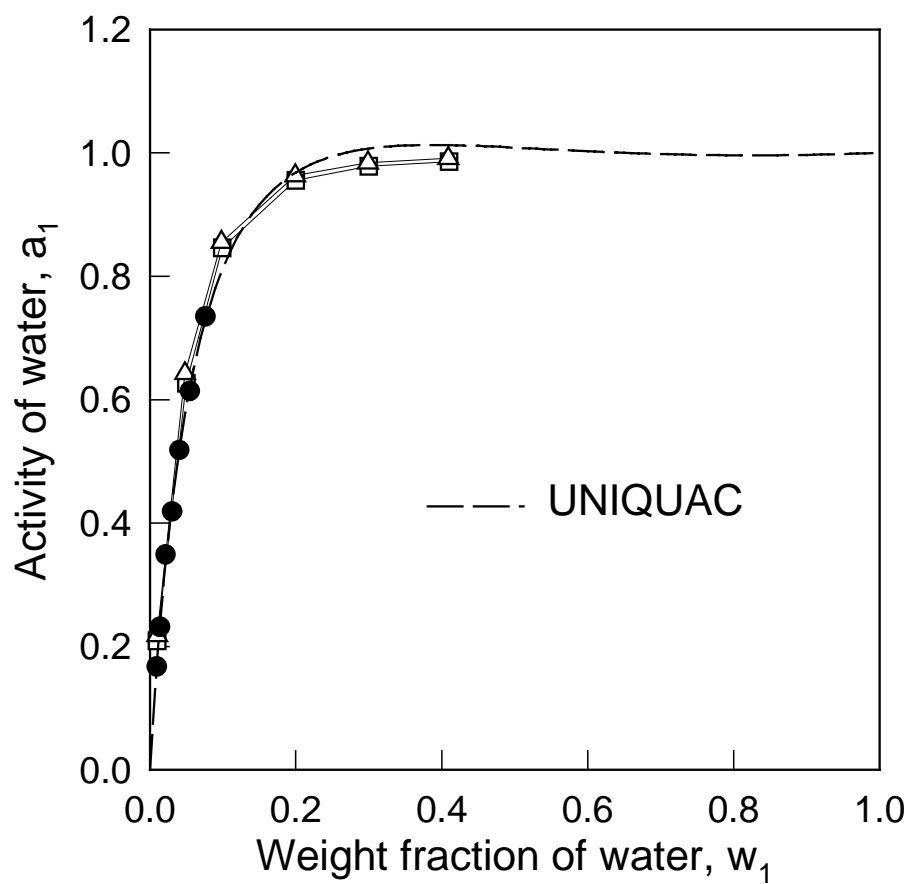


Figure 2. Measured and calculated activities of water in Poly(propylene glycol, Mn:400) at 303.15K : (●) sorption data measured in this work; (△) Malcolm et al. at 303.15K; (◻) Malcolm et al. at 323.15K.

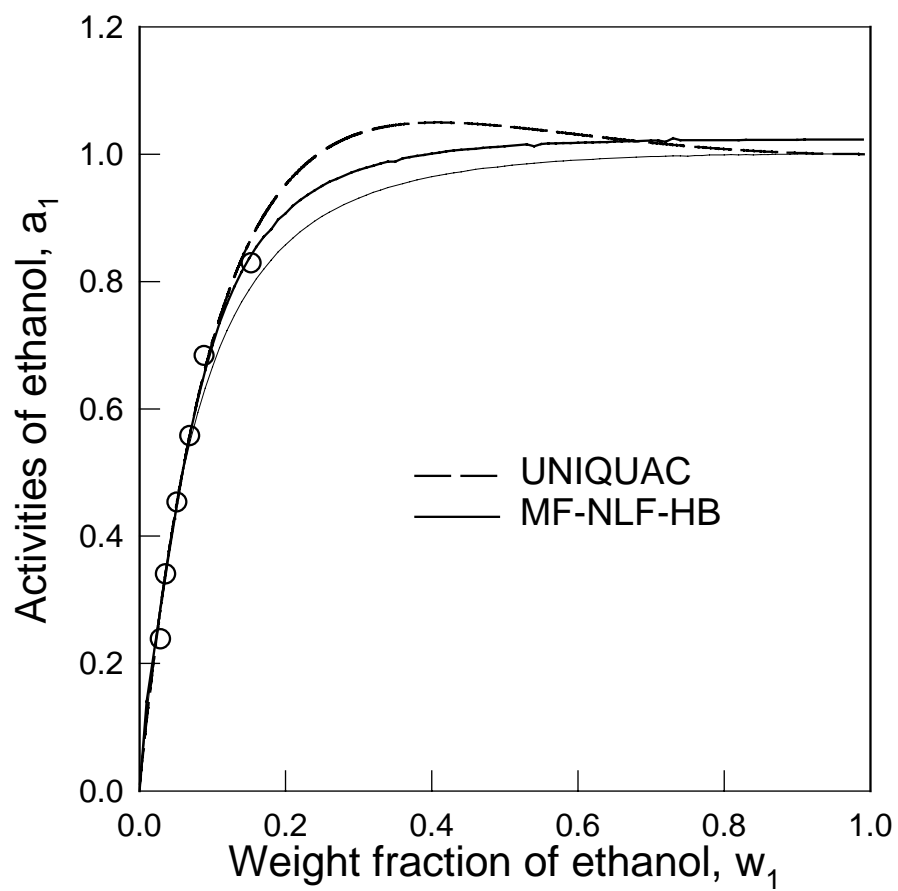


Figure 3. Measured and caculated activities of ethanol in Poly(ethylene oxide, Mn:600000) at 303.15K: (○) sorption data measured in this work.

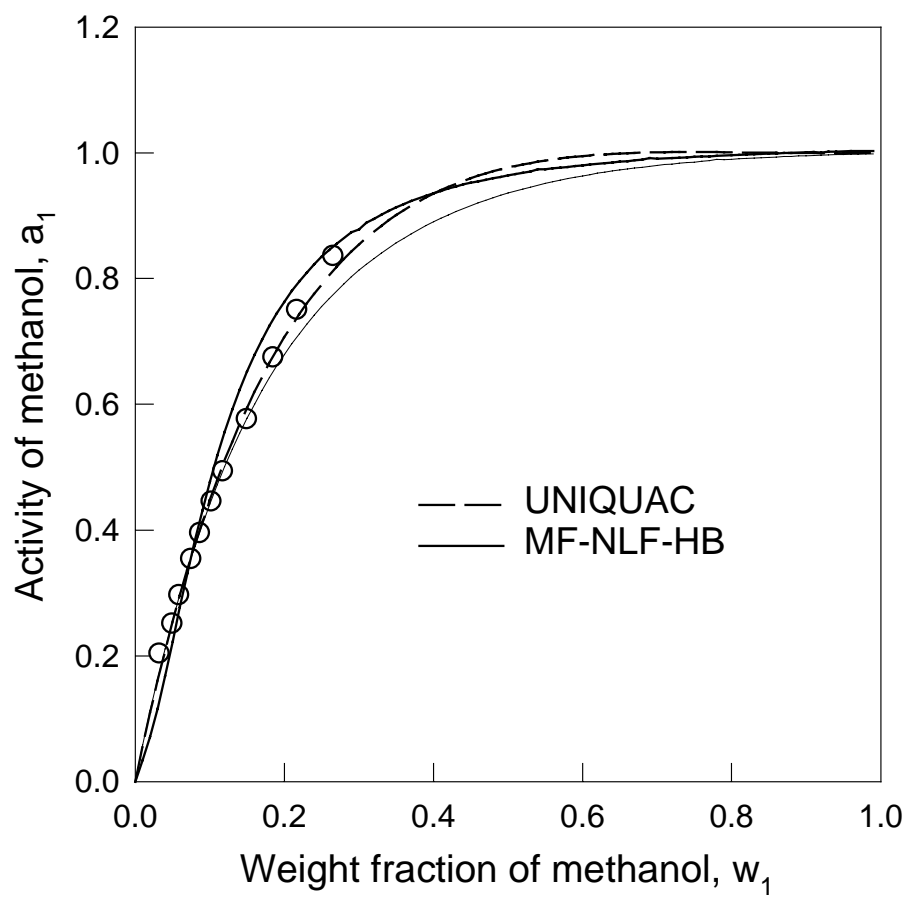


Figure 4. Measured and calculated activities of methanol in Poly(tetramethylene glycol, $M_n : 1400$) at 303.15K. : (○) sorption data measured in this work.

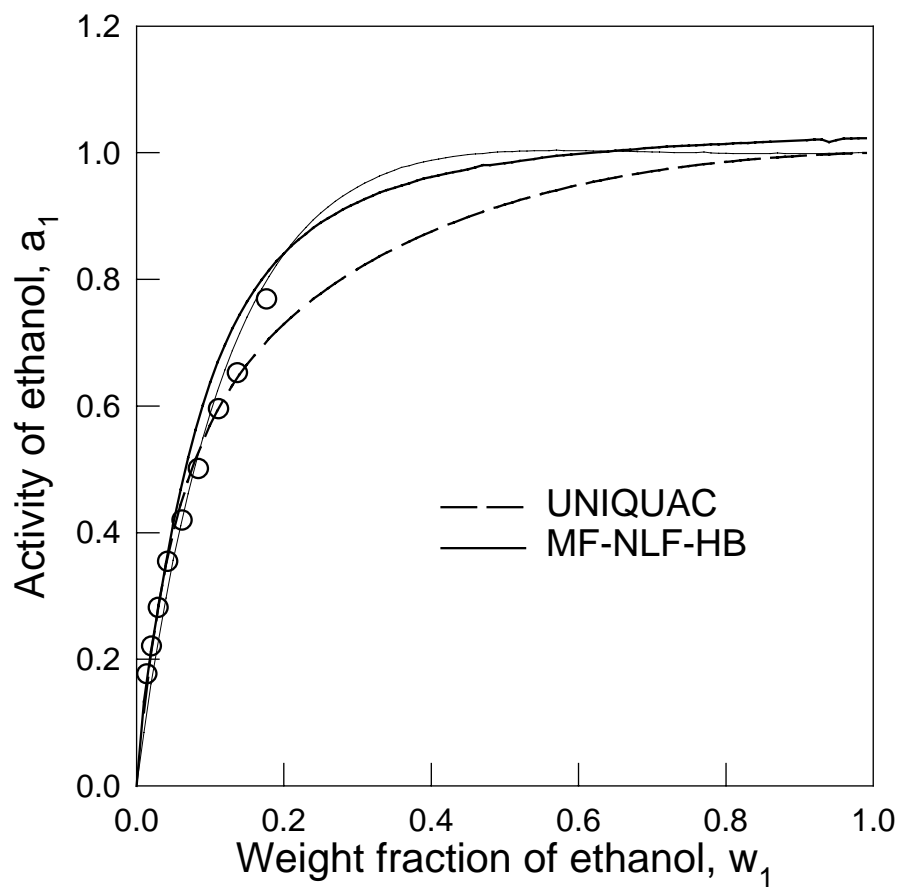


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EOS

Table 1. Measured Pressure and activities of solvent in solvent + polymer system

Polymer	Solvent	T ^a /K	w ₁ ^b	P ₁ ^c /kPa	a ₁	Polymer	Solvent	T ^a /K	w ₁ ^b	P ₁ ^c /kPa	a ₁
		303.1						303.1			
PEO	Water	5	0.0114	1.3866	0.2057	PTMG	Water	5	0.0023	1.1492	0.1523
			0.0219	1.8465	0.3140				0.0041	1.4772	0.2296
			0.0313	2.3598	0.4349				0.0072	1.7425	0.2921
			0.0453	3.0491	0.5971				0.0109	2.2105	0.4023
			0.0569	3.4664	0.6953				0.0148	2.5091	0.4726
			0.0777	3.9130	0.8004				0.0177	2.7998	0.5410
			0.1114	4.5956	0.9609				0.0254	3.3077	0.6605
		303.1						303.1			
PEO	Methanol	5	0.0850	5.1089	0.2348	PTMG	Methanol	5	0.0319	4.9863	0.2042
			0.1114	6.3128	0.2899				0.0491	6.0208	0.2517
			0.1430	8.0540	0.3697				0.0584	7.0101	0.2971
				10.309							
			0.1883	8	0.4729				0.0744	8.2660	0.3546
				12.625							
			0.3095	6	0.5786				0.0861	9.1659	0.3958
									10.252		
									0.1017	5	0.4460
									11.315		
PEO	Ethanol	5	0.0288	2.4905	0.2387				0.1171	1	0.4940
									13.129		
			0.0359	3.5557	0.3406				0.1489	6	0.5769
									15.285		
			0.0515	4.7356	0.4534				0.1846	4	0.6752
									16.945		
			0.0689	5.8289	0.5577				0.2164	3	0.7507
									18.829		
			0.0886	7.1487	0.6835				0.2650	1	0.8366
			0.1531	8.6780	0.8291						
						PTMG	Ethanol	5	0.0141	2.3598	0.1766
		303.1						303.1			
PPG	Water	5	0.0094	1.2172	0.1674				0.0205	2.8198	0.2207
			0.0137	1.4892	0.2315				0.0295	3.4557	0.2816
			0.0213	1.9865	0.3486				0.0424	4.2157	0.3542
			0.0304	2.2825	0.4183				0.0618	4.8996	0.4196
			0.0404	2.7064	0.5181				0.0841	5.7489	0.5007
			0.0549	3.1131	0.6138				0.1113	6.7408	0.5953
			0.0762	3.6264	0.7345				0.1371	7.3367	0.6522
		303.1						303.1			
PPG	Methanol	5	0.0354	5.1089	0.2123	PEG	n-Propanol	5	0.0246	1.8225	0.2593
			0.0555	6.8101	0.2903				0.0525	2.1945	0.3829
			0.0771	8.4126	0.3637				0.0829	2.5931	0.5344
				10.383							
			0.1043	1	0.4538				0.1264	3.0864	0.6402
				12.124							
			0.1353	3	0.5334				0.1805	3.5597	0.7615
				14.141							
			0.1693	5	0.6254				0.2354	4.1397	0.8662
									0.2354	4.1397	0.8662
		303.1						303.1			
PPG	Ethanol	5	0.0282	3.0851	0.2428						
			0.0460	4.0597	0.3360						
			0.0732	5.1329	0.4386						
			0.1049	6.3261	0.5525						
			0.1320	7.2861	0.6440						

^aT: temperature (±0.01°C). ^bw₁: weight fraction of solvent. ^cP₁: measured pressure of solvent (±0.001kPa).

Table 2. Estimated binary interaction parameters of UNIQUAC and MF-NLF-HB EOS

System	UNIQUAC		MF-NLF-HB	T/K
	A_{12}	A_{21}	λ_{12}	
PEG + n-propanol	-69.611	579.901	-0.0019	303.15
PEO + water	350.726	-77.654	-	303.15
PEO + methanol	351.136	-351.164	-0.1874	303.15
PEO + ethanol	118.217	237.305	-0.0520	303.15
PPG + water	-267.092	615.912	-	303.15
PPG + methanol	-221.279	344.110	-	303.15
PPG + ethanol	-186.145	572.231	-	303.15
PTMG + water	-327.823	1044.250	-	303.15
PTMG + methanol	498.551	-198.787	-0.0395	303.15
PTMG + ethanol	-289.722	735.196	-0.0189	303.15